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④ Mixtures based on polycarbonates having improved physical and chemical properties.

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EP-A- 173 358
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Description

The invention relates to a polymer mixture based on aromatic polycarbonate resin having two polymeric additives one of which is formed by 0.5-10% by weight, related to the said three components, of one or more graft copolymers having an elastomeric core which is built up for more than 50% by weight from a polymerised diene, optionally at least one intermediate phase of vinyl monomer polymerised thereon by grafting and a shell built up from a product of one or more monomers polymerised on the preceding phase by grafting and selected from the group consisting of: C₁-C₆ alkylacrylates, C₁-C₆ alkyl methacrylates, acrylic acid, methacrylic acid and mixtures of two or more of these monomers, with a cross-linking agent, and the other one is a block copolymer.

Such a mixture is known from EP-A-0173358. As a block copolymer is used in the said Application 0.5-4% by weight, related to the ternary mixture, of one or more partially hydrogenated block copolymers, consisting of at least two terminal polymer blocks of A monoalkenyl arylene having an average molecular weight of from 5,000-125,000 and at least one intermediate polymer block B of conjugated diene having an average molecular weight from 10,000-300,000, the terminal polymer blocks A constituting 8-55% by weight of the block copolymer, and not more than 25% by weight of the aromatic double bonds of the polymer blocks A and at least 80% by weight of the aliphatic double bonds of the polymer blocks B being reduced by hydrogenation.

As compared with the combination of aromatic polycarbonate with exclusively selectively hydrogenated block copolymer known from British Patent Specification 2,004,284, the mixtures of EP-A-0173358 show a better impact strength at low temperature, a better resistance to organic solvents and less delamination. However, it has been found in practice that these mixtures are not satisfactory in every respect. Although the impact strength has been improved, the value thereof at low temperature according to the Charpy test still leaves to be desired. Although furthermore the tendency to delamination is small, even this low tendency leads to insufficient depth of the colour in coloured products and sometimes also leads to imperfections in the surface. This latter disadvantage becomes more prominent in particular in the manufacture of big articles such as safety helmets, for which glaring colours are desired, and motor-car bumpers which upon injection molding may start to show unpleasant stripes on the surface.

It is to be noted that delamination on the other hand just promotes a good impact strength. The problem therefore was to further reduce delamination and on the other hand to still improve the impact strength.

The Applicants have surprisingly succeeded in solving this problem by replacing the block copolymer by another block copolymer and slightly adapting the ratios between the three components.

The invention therefore relates to a polymer mixture of the type mentioned in the opening paragraph which is characterised in that, related to the three components, the quantity of aromatic polycarbonate resin is 80-99% by weight and that the third component is formed by 0.5-10% by weight related to the three components, of a block copolymer of polycarbonate and polysiloxane.

The polymer mixture according to the invention preferably comprises 86-97% by weight of aromatic polycarbonate resin, 2-6% by weight of the graft copolymer and 1-8% by weight of the block copolymer.

WO-A-80/00084 describes blends of an aromatic polycarbonate and a block copolymer consisting of alternating segments of an aromatic polycarbonate and a polyorganosiloxane. The addition of a graft copolymer has not been described. The polymer mixture according to the invention has a better combination of flow properties, impact strength, at room temperature and at low temperatures as compared to the mixtures of WO-A-80/00084. The mixtures according to the invention show a greater consistency i.e. when remaking the same formulation there is less deviation in the properties. It seems that there is a better control of the morphology of the mixture according to the invention.

EP-A-0135794 describes polymer mixtures consisting of a polydiorganosiloxane-polycarbonate block copolymer (10-98 parts by weight), a rubbery polymeriseate (1-30 parts by weight) and a polyalkyleneterephthalate (0-50 parts by weight) (see claim 2). According to claim 3 the polydiorganosiloxane - polycarbonate block copolymer can be partly replaced by a polycarbonate. There are no examples dealing with a mixture of the three components as claimed in our invention. EP-A-0135794 suggests mixtures comprising a higher content of the polydiorganosiloxane - polycarbonate block copolymers as compared to the content of polycarbonate. The present invention clearly deals with mixtures comprising a higher quantity of polycarbonate as compared to the quantity of block copolymer. Mixtures comprising such high contents of the block copolymer as described in EP-A-0135794 behave as elastomers. The mixtures according to our invention are much stiffer.

The aromatic polycarbonate resin and the graft copolymer are of the same type as described in EP-A-0173358 and for a further description of these components reference may therefore be made to the said

EP-Application. As far as the polycarbonate resin is concerned, it will suffice to state that this is derived generally from a bivalent phenol and a carbonate precursor, for example, phosgene, halogen formate or carbonate ester, and that many bivalent phenols are suitable, among which bisphenol-A (BPA) is to be preferred, optionally in combination with a halogen-containing bivalent phenol to make the material flame-retarding. As is furthermore stated in EP-A-0173358 the aromatic polycarbonate resins preferably have an intrinsic viscosity of approximately 0.30-0.75 parts/g measured at 30 °C in p.dioxan. However, cross-linked polycarbonate resins are also suitable, for example, as described in United States Patent Specification 4,001,184.

As already stated, the graft copolymer has also been described elaborately in EP-A-0173358. Therefore, a few remarks will suffice here. The core of the graft copolymer is preferably built up from a styrene-butadiene copolymer having approximately 10-50% by weight of styrene and approximately 90-50% by weight of butadiene and having a molecular weight between 25,000 and 1,500,000, preferably 150,000-500,000. The core may also comprise a cross-linking agent. An optional second or further intermediate phase of the graft copolymer is obtained by graft polymerisation of one or more vinyl monomers, among which styrene is preferred. However, compounds, such as vinyltoluene, alpha-methyl styrene, halogenated styrenes and compounds such as acrylonitrile, methacrylonitrile and their halogenation products may also be used. The shell is obtained by graft polymerisation of one or more of the monomers already indicated hereinbefore for this phase, for example, methyl methacrylate, with a cross-linking agent. The cross-linking agent is conventionally used in a quantity of approximately 0.1-2.5% by weight related to the graft copolymer. As a cross-linking agent is used a polyalkenic unsaturated monomer with unsaturated groups which polymerise approximately at the same rate. This type of cross-linking monomers is generally known and examples hereof are ester of polyoles having two or more acryl- or methacrylic acid radicals, polyvinylbenzenes, vinylacrylate and vinyl methacrylate. Butylene diacrylate is preferably used. The presence of the cross-linking agent in the shell is necessary to obtain the desired shell-core structure.

The graft copolymer usually consists of 60-80 parts by weight of core, 10-20 parts by weight of optional intermediate phase and approximately 10-20 parts by weight of shell. A range of commercial products of this kind are marketed by Rohm and Haas Chemical Company under the tradename "ACRYLOID". A further description of the graft copolymers is to be found in addition in United States Patent Specification 4,180,494.

The block copolymer used according to the invention is a linear block copolymer of polycarbonate and polysiloxane. Such block copolymers are known *per se*. The polycarbonate blocks are preferably derived from bisphenol-A; the polysiloxane blocks are, conventionally, derived from siloxanes which are substituted by methyl-, vinyl- and/or phenyl groups, preferably in this case by methyl groups. The number of dimethyl siloxane units per block is preferably 7-11 and a suitable block copolymer of this type is the commercial product "LR 3320" of General Electric, which is a block copolymer of polybisphenol-A-polycarbonate and poly(dimethyl siloxane) with blocks of approximately 9 siloxane units. A description of suitable block copolymers can be found for example in US.2, 999,845, US.3,189,662, EP-A-0135794, EP-A-0146827 and EP-A-0193757.

As in EP-A-0173358, the polymer mixtures of the present invention may comprise, in addition to the above-described constituents, conventional additives, for example, pigments, flame-retarding additives, reinforcing agents, fillers, and stabilisers.

In this case also, the mode of preparation of the polymer mixtures is not critical. As in EP-A-0173358, it is to be preferred to mix the constituents and additives in a dry form, to extrude the resulting mixture and then to chop it to granules which can be subjected to the ultimate shaping process.

The invention will be described in greater detail in the ensuing specific examples.

EXAMPLES

A few mixtures according to the invention were prepared and compared with the preferred mixture of EP-A-0173358.

A homopolymer polycarbonate derived from 2,2-bis (4-hydroxyphenyl)propane (bisphenol-A) and phosgene and having a viscosity of 53 ml/g measured in di-chloromethane at 25 °C was used. As in the prior Application, the graft copolymer used was the commercial product ACRYLOID KM 653 and the above-mentioned Copel LR 3320 was used as the block copolymer, while in the comparative test according to EP-A-0173358 the Kraton G 1650 was used.

The mixtures in question were premixed for 3 minutes in a Papenmeyer high-speed mixer with stabilisers (per 100 parts of polymer mixture 0.1 part of organic phosphite, 0.2 parts of organic thioetherester and 0.3 parts of alkylarylpromionate) and 0.3 parts (per 100 parts of polymer mixture) of soot

pigment. The resulting mixture was melted and extruded on a 30 mm double-blade Werner-Pfleiderer extruder at 315-320° C and then granulated. Standardised test pieces were manufactured from the granulate on an injection moulding machine at 300° C, with which the following properties were determined:

5 Impact strength according to notch test by Charpy (DIN 53453). This determination was carried out at -
30° C.

Melt viscosity at two different shearing rates. The melts are non-Newton liquids and according as they show more thixotropy more delamination will also occur.

10 Chemical resistance with reference to two tests, namely impact strength according to the "Falling Dart" test at -20° C after dipping for 30 seconds at room temperature in fuel C (a mixture of iso-octane and toluene). In contrast with the prior Application, a scratch or notch has not been provided in the samples, so that, of course, the values are higher throughout than in the prior Application. The test apparatus cannot determine values higher than 220 J. Therefore, no fracture occurs at higher values and in the table below this is indicated as "NB". Finally, the elongation at fracture was determined, also at -20° C and without preceding deformation, also after dipping in fuel C at room temperature for 30 seconds. The tensile rate 15 was 100 cm/minute.

15 The examined compositions and the experimental results obtained are recorded in the table hereinafter.

	<u>Example</u>	<u>I</u>	<u>II</u>	<u>III</u>	<u>Comparative</u>
20	% Polycarbonate	94	92	90	94
	% Acryloid KM 653	4	4	4	4
25	% Copel LR 3320	2	4	6	-
	% Kraton G 1650	-	-	-	2

Experimental results

30	Notch impact value according to Charpy at -30° C (KJ/m ²)	25	36	37	13
	Melt viscosity at 300°C, Pa.s at shearing frequency				
35	115 s ⁻¹	348	327	327	472
	1500 s ⁻¹	256	250	244	272
40	Impact strength at -20° C according to Falling Dart method, J, after dipping in Fuel C, for 30 seconds,	4xNB	3xNB	3xNB	201
		200	218	210	204
45			217	190	201
					216
	5 samples				218

	<u>Experimental results</u>	<u>I</u>	<u>II</u>	<u>III</u>	<u>Comparative</u>
50	% elongation at fracture at -20° C after dipping for 30 seconds in Fuel C without preceding deformation;	14	23	37	20
55	elongation rate 100 cm/minute				

As appears from the above experimental results, the present polymer mixtures in the melt show a lower thixotropicity than the best blend of EP-A-0173358 which, therefore, means that the tendency to delamination is also smaller. Furthermore a strongly improved notch impact value according to Charpy is seen. The value for the Falling Dart test after dipping in a petrol-like liquid also shows a significant improvement and it appears from this experiment, and from the test regarding the elongation at fracture, that the chemical resistance of the present mixtures is at least approximately equally great or is better than that of the comparative mixture.

Claims

10. 1. A polymer mixture based on aromatic polycarbonate resin having two polymeric additives one of which is formed by 0.5-10% by weight, related to the said three components, of one or more graft copolymers having an elastomeric core which is built up for more than 50% by weight from a polymerised diene, optionally at least one intermediate phase of vinyl monomer polymerised thereon by grafting and a shell built up from a product of one or more monomers polymerised on the preceding phase by grafting and selected from the group consisting of: C₁-C₆ alkylacrylates, C₁-C₆ alkyl methacrylates, acrylic acid, methacrylic acid and mixtures of two or more of these monomers, with a cross-linking agent, and the other one is a block copolymer, characterised in that, related to the three components, the quantity of aromatic polycarbonate resin is 80-99% by weight and that the third component is formed by 0.5-10% by weight, related to the three components, of a block copolymer of polycarbonate and polysiloxane.
15. 2. A polymer mixture as claimed in Claim 1, characterised in that it comprises the three constituents in the following quantities:
20. 25. 86-97% by weight of aromatic polycarbonate resin;
2-6% by weight of graft copolymer and
1-8% by weight of block copolymer.
25. 3. A polymer mixture as claimed in Claim 1 or 2, characterised in that the block copolymer is built up from polycarbonate derived from bisphenol-A and polydimethylsiloxane.

Patentansprüche

30. 1. Polymermischung, basierend auf aromatischem Polycarbonatharz mit 2 polymeren Zusatzstoffen, von denen einer gebildet ist durch 0,5 bis 10 Gew.-%, bezogen auf die drei Komponenten, aus einem oder mehreren Ppropfcopolymeren mit einem elastomeren Kern, der zu mehr als 50 Gew.-% aus einem polymerisierten Dien aufgebaut ist, fakultativ wenigstens einer Zwischenphase aus darauf durch Ppropfen aufpolymerisiertem Vinylmonomeren und einem Mantel, der aus einem Produkt aus einem oder mehreren Monomeren, die auf die vorhergehende Phase durch Ppropfen aufpolymerisiert sind, und ausgewählt sind aus der Gruppe bestehend aus: C₁ - C₆ Alkylacrylaten, C₁ - C₆ Alkylmethacrylaten, Acrylsäure, Methacrylsäure und Mischungen aus zwei oder mehreren dieser Monomeren mit einem Vernetzungsmittel, und der andere Zusatzstoff ein Blockcopolymer ist, dadurch gekennzeichnet, daß in bezug auf die drei Komponenten die Menge des aromatischen Polycarbonatharzes 80 bis 99 Gew.-% beträgt, und daß die dritte Komponente durch 0,5 bis 10 Gew.-% eines Blockcopolymeren aus Polycarbonat und Polysiloxan, bezogen auf die drei Komponenten, gebildet ist.
35. 2. Polymermischung nach Anspruch 1,
dadurch gekennzeichnet, daß sie die drei Bestandteile in den folgenden Mengen enthält:
86 - 97 Gew.-% aromatisches Polycarbonatharz,
2 - 6 Gew.-% Ppropfcopolymeres, und
1 - 8 Gew.-% Blockcopolymer.
40. 3. Polymermischung nach Anspruch 1 oder 2,
dadurch gekennzeichnet, daß das Blockcopolymer aus Polycarbonat aufgebaut ist, welches von Bisphenol A und Polydimethylsiloxan abgeleitet ist.

Revendications

1. Mélange de polymères à base de résine de polycarbonate aromatique et comprenant deux adjuvants polymères, dont l'un est constitué par 0,5-10 % en poids, par rapport aux trois composants mentionnés, d'un ou de plusieurs copolymères greffés comportant un noyau d'élastomère constitué pour plus de 50 % en poids d'un diène polymérisé, éventuellement au moins une phase intermédiaire de monomère vinylique polymérisé par-dessus par greffage, et une coque constituée du produit de polymérisation d'un ou plusieurs monomères polymérisés par greffage sur la phase précédente et choisis dans le groupe que constituent les acrylates d'alkyle en C₁-C₆, les méthacrylates d'alkyle en C₁-C₆, l'acide acrylique, l'acide méthacrylique et les mélanges de deux de ces monomères ou plus, avec un agent de réticulation, et l'autre adjuvant est un copolymère séquencé, mélange caractérisé en ce que, par rapport aux trois composants, la proportion de résine de polycarbonate aromatique vaut 80-99 % en poids et en ce que le troisième composant est formé de 0,5-10 % en poids, par rapport aux trois composants, d'un copolymère séquencé de polycarbonate et de polysiloxane.
- 15 2. Mélange de polymères tel que revendiqué dans la revendication 1, caractérisé en ce qu'il contient les proportions suivantes des trois composants:
86-97 % en poids de résine de polycarbonate aromatique,
2-6 % en poids de copolymère greffé, et
1-8 % en poids de copolymère séquencé.
- 20 3. Mélange de polymères tel que revendiqué dans la revendication 1 ou 2, caractérisé en ce que le copolymère séquencé est constitué d'un polycarbonate dérivé du bisphénol A et d'un polydiméthylsiloxane.

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